# M.Sc. 4th Semester Examination, 2021

## CHEMISTRY

## (Physical Chemistry Special)

## Paper: CHEM 401E

## Course ID: 41451

**Time: 2 Hours** **Full Marks: 40**

*The figures in the margin indicate full marks.*

*Candidates are required to give their answers in their own words as far as practicable.*

1. Answer *any five* of the following questions: 2×5 = 10

a) What is the wavelength of an $H^+$ ion (mass = $1.7\times10^{-27}$ kg) moving with a velocity equal to 1/100th of light?

b) If $\Phi_1$ and $\Phi_2$ are two degenerate eigenfunctions of the linear operator $\hat{H}$, show that $\psi = C_1\Phi_1+C_2\Phi_2$ is an eigenfunction of $\hat{H}$ with the same eigenvalue as that for $\Phi_1$ and $\Phi_2$.

c) Calculate the length of a one dimensional box for which the difference between the lowest energy levels of a molecule becomes comparable to its average kinetic energy at a given temperature.

d) Show that $\psi_1 = x$ and $\psi_2 = x^2$ are orthogonal over the interval $-k \le x \le k$ [k is a constant].

e) Determine the degree of degeneracy of the energy level $\frac{17h^2}{8ma^2}$ of a particle in a cubical box.

f) For a particle in the state n=1 of a one dimensional box of length L, find the probability that the particle is in the region $0 \le x \le L/4$.

g) A particle with mass $m_1$ is restricted to move in a circular path. Set up the Schrödinger equation for this rotator.

2. Answer *any four* of the following questions: 5×4 = 20

a) Show that $\left[\widehat{L_{x,}}\widehat{L_y}\right] = \frac{ih}{2\pi}\widehat{L_z}$. 5

b) Explain that $L_+$ or $L_-$ is not Hermitian, but $L_+L_-$ or $L_-L_+$ is. 5

c) What are spherical harmonics? Show that they are eigenfunctions of both $\widehat{L^2}$ and $\widehat{L_z}$ , L being the orbital angular momentum. What are the eigenvalues for each of the two operators? 1+2+2 = 5

d) Provide the following information for an electron in 3d orbital.

(i) The magnitudes of the vectors $\hat{L}$ and $\hat{S}$.

(ii) The possible values of the quantum numbers $j$ and $m_j$.

(iii) The magnitudes of the vectors $\vec{J}$ and their z-components. 1.5+1.5+2 = 5

e) Determine the term symbols for $np^4$, $np^5$, $d^1$, $d^3$, $d^4$ systems. 5

f) (i) Draw the energy level diagrams for $^3D$ and $^3P$ states.

(ii) What are the magnitudes of total orbital, total spin and total angular momenta for the ground state term $^4F$ of vanadium? 3+2 = 5

3. Answer *any one* of the following question: 10×1 = 10

a) Define ladder operator. Derive the relations, $[L^2, L_\pm] = 0, \left[L_{z,}L_\pm\right] = i\hbar\widehat{L_\pm}$ and $[L_+, L_z] = 2\hbar\widehat{L_z}$ 1+3+3+3 = 10

b) (i) Consider a trial function, ψ = x(a-x) for a particle in a one-dimensional box of length a. Show that this function satisfies the boundary conditions. Apply the variation method to get an upper bound to the ground state energy of the particle, and compare the result with true value given in, $E = \frac{h^2}{8ma^2}$ . 5

(ii) A trial function to a given system is given by, $\Phi = N(\psi_1+\lambda\psi_2)$, where N is the normalization constant and λ is a variational coefficient to be determined. If $\psi_1$ and $\psi_2$ are arbitrary basis functions, show how λ can be determined by the variation method. 5

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